**ELECTRON CONCENTRATION AND PHASE
STABILITY IN NbCr₂-BASED LAVES
PHASE ALLOYS**

May 12, 1997

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ABSTRACT

Phase stability in NbCr_2 -based transition-metal Laves phases was studied, based on the data reported for binary X-Cr, Nb-X, and ternary Nb-Cr-X phase diagrams. It was shown that when the atomic size ratios are kept identical, the average electron concentration factor, e/a , is the dominating factor in controlling the phase stability of NbCr_2 -based transition-metal Laves phases. The e/a ratios for different Laves polytypes were determined as follows: with $e/a < 5.76$, the C15 structure is stabilized; at an e/a range of 5.88-7.53, the C14 structure is stabilized; with $e/a > 7.65$, the C15 structure is stabilized again. A further increase in the electron concentration factor ($e/a > 8$) leads to the disordering of the alloy. The electron concentration effect on the phase stability of Mg-based Laves phases and transition-metal A_3B intermetallic compounds is also reviewed and compared with the present observations in transition-metal Laves phases. In order to verify the e/a /phase stability relationship experimentally, additions of Cu (with $e/a = 11$) were selected to replace Cr in the NbCr_2 Laves phase. Experimental results for the ternary Nb-Cr-Cu system are reported and discussed in terms of the correlation between the e/a ratio and phase stability in NbCr_2 -based Laves phases. A new phase was found, which has an average composition of Nb-47Cr-3Cu. Within the solubility limit, the electron concentration and phase stability relationship is obeyed in the Nb-Cr-Cu system.

I. INTRODUCTION

Laves phases with AB_2 compositions generally crystallize into one of the three topologically close-packed structures: cubic C15 – $MgCu_2$ structure, hexagonal C14 – $MgZn_2$ structure, and dihexagonal C36 – $MgNi_2$ structure.¹ Although Laves phases are generally stabilized by the size-factor principles, that is, the atomic size ratio, R_A/R_B , is ideally 1.225, with a range of 1.05-1.68 usually observed, the stability of each crystalline structure is also influenced by the electron concentration factor (e/a).^{2,3} In fact, the electron concentration factor becomes clearly important when the atomic size factors are favorable. The classic work by Laves and Witte^{2,3} showed that for several quasi-binary alloy systems involving $MgCu_2$ and $MgZn_2$, with increasing valence electron concentration, the three Laves types, $MgCu_2$, $MgNi_2$, and $MgZn_2$, exist in that order. For transition-metal Laves phases, the average electron concentration and the d-band hole number were successfully used to correlate the crystal structure by Bardos, Gupta and Beck,⁴ and Watson and Bennet.^{5,6}

Transition-metal Laves phases are currently being considered for many practical applications, e.g., $(Hf,Zr)V_2$ as superconducting material, $Zr(Cr,Fe)_2$ as hydrogen storage material, etc. More recently, HfV_2 -, $HfCr_2$ - and $NbCr_2$ -based two-phase alloys⁷⁻¹³ are being developed for high-temperature structural uses, because of their retention of good mechanical properties at elevated temperatures. However, their low ductility and brittle fracture characteristics at ambient temperatures are the main concerns for structural applications of these materials.

One attractive way to improve the deformability of complex Laves phases is to control their crystalline structure in a way that stress-assisted phase transformation and/or mechanical twinning can be introduced during plastic deformation.^{14,15} It is thus important to know the factors governing the phase stability in transition-metal Laves alloys.

In this investigation, a number of binary and ternary phase diagrams were surveyed, and

the phase stability criteria in the NbCr₂-based Laves phase systems, binary X-Cr and Nb-X and ternary Nb-Cr-X, were studied. The electron concentration factor (e/a) was identified as the key parameter in controlling the C14/C15 phase stability in NbCr₂-based transition-metal Laves alloys, similar to the effect of electron concentration on the phase stability in Mg-based Laves phases and transition-metal A₃B intermetallic alloys. Furthermore, the Laves-phase stability in the ternary Nb-Cr-Cu system was studied experimentally to verify the observed electron concentration/phase stability relationship. The results are discussed in terms of both solubility limit and electron concentration in the Nb-Cr-Cu system.

II. LAVES PHASES IN BINARY X-Cr AND Nb-X SYSTEMS

Since Laves phases are size compounds, we should choose the X elements in the X-Cr systems with an atomic radius close to Nb, and X elements in the Nb-X systems with an atomic radius close to Cr. In this scheme, we can easily separate the e/a factor from the atomic size factor in controlling the phase stability. According to this scheme, the X elements selected in the X-Cr systems are Ti, Ta, and Nb, and the X selected in the Nb-X systems are Cr, Mn, Fe, Co, Ni, and Cu. The selection of atom size is based on the consideration of the Goldschmidt radius with a coordination number (CN) of 12.¹⁶ With a minimum disturbance of the atomic size factor, the electron concentration ratio, e/a , should become a dominant factor in controlling the phase stability of the binary Laves phases. Here, the e/a ratio is defined as the average number of electrons per atom outside the closed shells of the component atoms. According to this definition, the e/a ratio of a transition element is the number of electrons ($s + d$ electrons) outside its inert gas shell.

Table 1 lists the Goldschmidt radii (CN = 12), and the e/a ratios of all the alloy components, together with the existing Laves phases observed in the binary X-Cr and Nb-X systems. It is interesting to note that Ti and Ta have atomic radii close to Nb, and thus, they are postulated to substitute for Nb in the NbCr₂ Laves phase. Mn, Fe, Co, Ni and Cu have atom sizes close to Cr and occupy the Cr positions in the NbCr₂ Laves phase. From

the binary X-Cr and Nb-X phase diagrams,¹⁷ we can determine if the XCr₂ or NbX₂ Laves phase exists in the X-Cr and Nb-X systems, as indicated in Table 1. Also, the homogeneity ranges of XCr₂ or NbX₂ Laves phases can be determined from the binary phase diagrams. The homogeneity range (or mutual solubility) is defined here as the difference between the maximum and minimum atomic percents of A in the AB₂ phase. Corresponding to the homogeneity ranges, we can calculate the e/a ranges for the different binary Laves phases using the e/a ratios for various transition elements listed in Table 1 according to the following equation:

$$(e/a)_{\text{Laves-phase}} = \sum_i [(e/a)_i \times (\text{at.}\%)_i] \quad (1)$$

where $i = i_{\text{th}}$ alloying element.

The binary Laves phase, R_A/R_B ratio, homogeneity range (%A range), e/a range, and corresponding Laves phase structure are listed in Table 2. Since temperature is also a factor affecting the phase stability of Laves phases, polytypes may exist at different temperatures in some binary systems. To minimize or eliminate the temperature effect, the Laves structure investigated in the present study is the one stabilized at lower temperatures, if more than one Laves structure exist in the binary system. Also note that no Laves phases were observed in the binary Nb-Ni and Nb-Cu systems, and that the calculation of the e/a ratio was based on the imaginary "NbNi₂" and "NbCu₂" phases.

In Table 2, the R_A/R_B ratios were maintained at approximately the same value for all of the Laves phases. The C15 structure was stabilized at low values of e/a (≤ 5.70) in Table 2. A change of the structure from C15 to C14 occurred when e/a was equal to or greater than 6.20. Interestingly, C15 was stabilized again when e/a was equal to or greater than 7.67. As the e/a value further increases (≥ 8.34), no ordered Laves phases exist.

III. LAVES PHASES IN TERNARY Nb-Cr-X SYSTEMS

As postulated in the previous section, Ti and Ta occupy the Nb lattice sites in the NbCr₂ Laves phase. From the ternary Nb-Cr-Ta and Nb-Cr-Ti phase diagrams,¹⁸ Ti or Ta can substitute for Nb from 0% to 100% without changing the C15 structure of NbCr₂. This behavior further confirms our above postulation that Ti and Ta will mainly substitute for Nb in the NbCr₂ Laves phase as the atomic radii of Ta, Ti and Nb are essentially the same. For Mn, Fe, Co, Ni, and Cu, they are postulated to substitute for Cr in the NbCr₂ phase. There is no ternary Nb-Cr-Mn phase diagram reported so far, and the ternary Nb-Cr-Cu phase diagrams are incomplete, with the reported data mainly concentrated at the copper-rich corner. On the other hand, the Nb-Cr-Co, Nb-Cr-Fe and Nb-Cr-Ni phase diagrams have been reported in the literature.^{18,19} From these phase diagrams, common trends were observed: Fe, Co and Ni have some solubility in the NbCr₂ phase without changing the C15 structure. However, above a certain critical amount of Fe, Co or Ni added to the stoichiometric NbCr₂ to substitute for Cr, a phase modification from C15 to C14 was observed (Table 3). The C14 phase is stable over a wide range of Fe, Co or Ni content. For the Nb-Cr-Co system, a further increase in the Co content results in the reappearance of the C15 structure,¹⁹ as shown in Table 3.

The stability ranges of C14 and C15 phases in the ternary Nb-Cr-X systems at around 1000°C are summarized in Table 3, together with the corresponding e/a values that were calculated using Equation 1. This temperature range was chosen due to the lack of pertinent ternary phase diagrams at lower temperatures. From Table 3, it should be noted that the solubility of Fe, Co, and Ni in NbCr₂ with the C15 structure decreases in the order of Fe, Co, and Ni. However, the e/a ratios corresponding to the change of the C15 to C14 structure are almost identical (i.e., 5.75, 5.76, and 5.77) for the different systems of Nb-Cr-Fe, Nb-Cr-Co and Nb-Cr-Ni, respectively. This trend implies that the average electron concentration may play a key role in determining the C15/C14 phase stability. The average maximum e/a for the C15 structure is 5.76 and the average minimum e/a ratio to stabilize the C14 structure is about 5.88. A transition from C14 to C15 was observed in the Nb-Cr-

Co system when e/a was equal to or greater than 7.65. Note that the transition from C14 to C15 was also found in the binary Laves phases, as shown in Table 2.

IV. EFFECT OF e/a ON LAVES-PHASE STABILITY

Laves phases are compounds of the general formula AB_2 , with three crystal types, C15, C36, and C14, generally observed. There is a marked similarity among the three structures. These consist of double layers of hexagonal arrays of A atoms surrounded by tetrahedra of the B elements. One stacking layer consists of 4 sub-layers, and thus, they are called quadruple layers. The cubic C15 structure consists of such layers stacked ABCABC, while the C14 consists of such layers stacked ABABABAB. C36 may be regarded as a transitional phase between the C15 and C14 structures with a stacking of these layers ABACABAC. Laves phases are size compounds, and therefore, the size difference between A and B atoms is predominant in stabilizing the Laves phase. Since we purposely chose some alloying elements with roughly the same atomic sizes with either Cr or Nb (see Tables 1 and 2), the atomic size difference between A and B is similar in the AB_2 Laves phases investigated. This approach simplifies our analysis, since we can separate the other factors from the size factor in stabilizing different Laves phase structures. Also, we only chose transition metals to form Laves phases, which made it ideal to study the e/a effect on the Laves-phase stability. In transition metals, filling the d-band is important for the phase stability.

In Laves and Witte's studies,^{2,3} ternary Mg-based systems were selected, and a valence electron concentration rule was found to control the occurrence of various Laves structures, with C15 stabilized at low e/a values, C14 stabilized at high e/a values, and C36 in between, see Fig. 1. The correlation is reasonably good; however, both non-transition and transition metals were involved in forming some Laves phases in their study, making it difficult to analyze the valence electron concentrations in the alloys. This difficulty results from the fact that for a transition element, the valence electron number is not a constant value, but varies in different systems. This behavior may contribute to the scattering in the

critical e/a values corresponding to the phase transitions for the different ternary systems, as shown in Fig. 1, e.g., there is an overlapping of the C14 and C36 structures in the valence electron concentration ranges between 1.8 and 2.0.

In the present evaluation, all the elements chosen to form Laves phases were transition metals. Instead of using the valence electron concentration, the average electron concentration was chosen for correlation purposes. This concept of average electron concentration has been successfully used to obtain a correlation between the e/a value and the phase stability in some transition metal alloy systems.^{4,5,20-24} If we combine the data in Tables 2 and 3 for both binary and ternary alloy systems, we can clearly demonstrate the e/a effect on the phase stability (C14/C15) in NbCr₂-based Laves alloys (see Fig. 2).

At e/a values lower than 5.76, the C15 structure was stabilized for both binary and ternary Laves alloys (Fig. 2). By increasing e/a to 5.88, the C14 structure was stabilized. Over the e/a range of 5.88-7.53, the C14 structure is more stable than the C15 structure. This trend is similar to that observed in the Mg-based Laves phases,^{2,3} where the C15→C36→C14 phase modification was observed with an increasing e/a value (Fig. 1). However, for the Mg-based Laves phases, this should be considered as a tendency, as it is impossible to classify the compounds in terms of their e/a ratios, as discussed before.

In ternary NbCr₂-based Laves phases, the e/a ratio for the C15/C14 phase boundaries is very precise, with C15 existing at $e/a \leq 5.76$, and C14 occurring at $e/a \geq 5.88$ (Fig. 2). This may be associated with the fact, as mentioned previously, that all the components of the ternary NbCr₂-based Laves phases are transition metals. The region between the two single phase regions should be a two phase mixture of C14 and C15 from thermodynamic considerations. However, in reality, it is possible to obtain different intermediate structures, due to the metastable transformation of the one to the other and/or the low chemical free energies of some intermediate structures. For example, the C36 phase exists in some Mg-based Laves alloys, as shown in Fig.1.

Moreover, Komura and his coworkers have shown that additional Laves-type structures exist in at least some of these quasi-binary Mg-based systems.²⁵⁻²⁷ The hexagonality of the stacking arrangement decreases, and then increases with increasing valence electron concentration, i.e., as the valence electron concentration increases, the percentage of hexagonality observed changes in the following sequence of 50→33→0→50→57→60→62→66→71→75→100.

However, no existence of C36 and other intermediate structures were indicated in the reported phase diagrams of binary and ternary NbCr₂-based systems between the C14 and C15 phase fields. This is probably due to the fact that no detailed work on crystal structures was undertaken to determine the various intermediate structures in this region. Thus, it is postulated that at least in some of the NbCr₂-based Laves-phase systems, C36 and other intermediate structures may exist in the *e/a* regime of 5.76-5.88, probably around 5.7-5.9 due to the variability in the literature data. In fact, a C36 phase was detected in a recent study of the transition-metal Nb-Cr-Fe system.¹⁵ Even though it is difficult to calculate the exact *e/a* value for the C36 Laves phase, since that system is basically a dual-phase alloy with a Nb solid solution and a Laves phase, it does indicate that it is possible to stabilize at least the C36 structure at certain *e/a* ratios.

Over the *e/a* range considered, the atomic size difference has no effect on the *e/a* correlation with the phase stability in both binary and ternary NbCr₂-based systems. Actually, the solubility of Fe, Co and Ni in NbCr₂ has different values, yet the same critical *e/a* value is yielded, with respect to the change of the crystal structure from C15 to C14 (Fig. 2). These observations may result from the fact that the atomic size difference (R_A/R_B) is kept similar in our investigation. However, the atomic size difference may affect the homogeneity range of the NbCr₂-based Laves phase, as shown in Fig. 3. No good correlation between the R_A/R_B ratio with the homogeneity range can be inferred from Fig. 3. Note that all the binary Laves phases considered show a certain amount of homogeneity range, a result consistent with the geometry analysis of solubility ranges in Laves phases

performed by Thoma and Perepezko.²⁸

The effect of the average electron concentration on phase stability has been shown in some transition-metal A_3B intermetallic compound systems, usually with a very good correlation obtained.²⁰⁻²² For example, Liu found that the stacking character of the $(Fe, Co, Ni)_3V$ ordered alloys can be altered systematically by controlling the e/a ratio of the alloys²⁰ (see Fig. 4). Here, the basic A_3B one-layer structure is the (111) close-packed plane, which is different from the case for Laves phases, where a quadruple layer forms a close packed plane. Different ordered structures can be obtained depending on their stacking sequence. Similar to our observation in Laves phases, as e/a increases, the stacking character changes from purely cubic, through a mixture of cubic and hexagonal, to purely hexagonal. However, the critical e/a ratios for stabilizing the ordered face-centered cubic (f.c.c.) structure (≤ 7.89) and ordered hexagonal close-packed (h.c.p.) structure (≥ 8.54) in A_3B compounds are different from those for stabilizing the cubic C15 structure (≤ 5.76) and hexagonal C14 structure (≥ 5.88) in the $NbCr_2$ -based transition-metal Laves phases. Also, similar to Mg-based Laves phase alloys, different ordered mixtures of cubic and hexagonal layers were obtained between the cubic and hexagonal structures for the A_3B ordered alloys, i.e., Co_3V with $e/a = 8$ shows 33.3 percent hexagonality and $(Co, Ni)_3V$ with $e/a = 8.43$ shows 66.7 percent hexagonality. All the results indicate that the average electron concentration factor has a determinate effect on the phase stability of transition-metal intermetallic compounds. The reason leading to such a correlation is not clear now; however, the phase transition in transition metals is known to be related to the filling of an appropriate Brillouin zone^{20,22} and can be predicted from the ground state phase stability map.²⁹

From Fig. 2 and Table 3, we can also see that for the Nb-Cr-Co system, when the e/a ratio increases further to 7.65, the C15 structure was stabilized again over the C14 structure. Similarly in the binary systems, there is a C14→C15 transition when e/a is greater than 7.65 (Fig. 2 and Table 2). This structure modification of C14 to C15 with a further increase in the e/a ratio has been observed in a number of transition-metal Laves phases.³⁰

It is a general trend, rather than an exception. In the ternary Nb-Cr-Fe system, we cannot observe such a C14 to C15 transition, since we are unable to obtain an e/a ratio higher than 7.6 in this system (Fig. 2 and Table 3). No NbNi₂ (with $e/a = 8.34$) and NbCu₂ (with $e/a = 9$) Laves phases exist in binary Nb-Ni and Nb-Cu systems (Table 2), a fact consistent with the observation by Bardos et al.⁴ that at $e/a > 8$, a disordered structure is stabilized over the Laves phase in transition-metal systems. Also in agreement with Bardos et al., the maximum e/a ratio for the Laves phases in the Nb-Cr-Ni system is around 8. However, no C14→C15 transition in the Nb-Cr-Ni system was reported at e/a ratios > 7.65 , possibly due to the fact that many ternary phase diagrams containing Laves phases are inaccurate with regard to the identification of C14/C36/C15 structures. Note that as discussed before, it is postulated that C36 and other intermediate structures may exist between C14 and C15 structures at $7.65 > e/a > 7.53$.

If the electron concentration e/a correlation with the phase stability (Fig. 2) is a rule operating in the NbCr₂-based transition-metal alloy systems, it will be possible to change from C15 to C14 and from C14 to C15 again by adding Cu ($e/a=11$) into NbCr₂ to substitute for Cr, i.e., by varying the e/a ratio in the alloy. So far, no data are available for the ternary Nb-Cr-Cu system. Thus, the Nb-Cr-Cu system was chosen in this investigation, and the results in this system are reported in the next section.

V. EXPERIMENTAL STUDY OF THE e/a CORRELATION

From Table 1, Cu has eleven outshell electrons (the highest e/a). Thus, the addition of Cu to substitute for Cr ($e/a = 6$) in NbCr₂ is very effective in increasing the average electron concentration. By a systematic replacement of Cr with Cu, it is possible to see a whole spectrum (e.g., C15→C14→C15) of changes in the crystal structure of the Laves-phase based Nb(Cr,Cu)₂ compositions. A series of pseudo-binary Nb(Cr,Cu)₂ alloys with 1, 3, 5, 10 at % Cu were produced by replacing Cr with Cu, while keeping the percentage of Nb constant. The nominal chemical compositions in the atomic percentage of the alloys studied in this work are Nb-65.6Cr-1Cu, Nb-63.6Cr-3Cu, Nb-61.6Cr-5Cu, and Nb-56.6Cr-

10Cu, which correspond to average electron concentrations of 5.71, 5.81, 5.91 and 6.16, respectively. These four alloys are in the C15 region, the C15/C14 transition region, and the C14 region, respectively, according to the prediction of Fig. 2.

All the alloys of about 50 grams were prepared by arc-melting techniques using starting materials of 99.8% Nb, 99.99% Cr, and 99.99% Cu. An excess amount (typically 1%) of Cr was added to compensate for the evaporation loss of Cr during melting. Arc-melting was carried out in a chamber which was evacuated by a mechanical pump and flushed with ultra-high purity (UHP) argon gas four or five times, and finally backfilled with UHP argon gas. A Zr sample was melted prior to melting the alloy charge each time in order to getter the oxygen in the chamber. The arc-melting was done using a thoriated tungsten electrode on a water-cooled copper hearth. Each ingot was inverted and remelted at least 7 times to ensure macroscopic compositional homogeneity. The material was heat-treated in vacuum at 1400°C for 120 hours, then slowly cooled in the furnace.

An electron microprobe equipped with wavelength-dispersive spectrometry (WDS) was used to identify the microstructure and the chemical compositions of various phases in the heat-treated specimens. X-ray diffraction measurements were made using a Scintag XD2000 diffractometer with the Cu K_{α} ($\lambda = 0.15406$ nm) radiation.

X-ray diffraction results show that the Laves phase after the addition of up to 10 at. % Cu maintains its original C15 structure, i.e., no phase transition is observed for all the alloys investigated. As an example, Fig. 5 shows the indexed C15 diffraction pattern for the Nb-61.6Cr-5Cu alloy. This seems to contradict our e/a correlation with phase stability, as the addition of 5 at % Cu should stabilize the C14 structure according to Fig. 2. Optical microscopy shows that more than one phase are present in the 5 at % Cu alloy, see Fig. 6(a). Using the electron microprobe, it was found that four phases coexist in this alloy, see Fig. 6(b).

Table 4 summarizes the results of the electron microprobe analyses. Here, the matrix is the

Laves phase with an average composition of Nb = 33.9, Cr = 64.8 and Cu = 1.3. From this composition, it can be seen that Cu indeed substitutes for Cr in the NbCr₂ phase. The bright phase has a formula of roughly AB assuming again that Cu substitutes for Cr in the lattice. This phase is possibly a σ phase, which does not exist in the Cr-Nb binary system. It is interesting to note that the addition of 3 at % Cu stabilizes this bright phase. This new phase has not been reported before and deserves further investigations. The dark phase and the gray phase are Cu and Nb solid solutions, respectively. The solubility of Nb and Cr in Cu is only 0.1 and 2.55%, respectively. The gray phase is a Nb solid solution with 0.44 % Cu and 4.19% Cr.

The low solubility of Cu in the NbCr₂ phase, i.e., 1.3 at. %, is a rather surprising finding. The average electron concentration of the Laves phase in the Nb-61.6Cr-5Cu alloy can be calculated to be 5.73. Since an average electron concentration of 5.73 is still in the C15 range, as shown in Fig. 2, no phase transition will be expected. Thus, the experimental results are, in fact, consistent with our e/a correlation prediction, i.e., when $e/a < 5.76$, the C15 structure is stabilized. The question arising here is why the solubility of Cu in the NbCr₂ phase is so low, since its atomic radius is favorable for it to substitute for Cr (Table 1). According to Hume-Ruthery's rules on the solubility of a solid solution, three parameters, namely, e/a , atomic radius, and electronegativity, are dominating factors in determining the solubility limit. Since both the e/a and electronegativity differences between Cr and X in the binary NbX₂ system are the largest for Cu, the low solubility of Cu in the NbCr₂ phase is believed to be a combination of unfavorable e/a and electronegativity for Cu to be dissolved in Cr.

The Nb-61.6Cr-5Cu alloy was also heat-treated in the following way to achieve an equilibrium condition at 1000°C: 1400°C for 120 hours, 1000°C for 120 hours, followed by water quenching. X-ray diffraction results show the diffraction pattern of C15, while the optical microstructure of the alloy is similar to that after furnace cooling, see Fig. 6(a). These results also indicate that C15 is the stable structure in this Nb-Cr-Cu alloy at 1000°C. Moreover, the above results indicate that within the solubility limit, the crystal structure of

the Nb-Cr-Cu alloy obeys the e/a and phase stability relationship presented in Fig. 2.

VI. CONCLUSIONS

Binary X-Cr and Nb-X, and ternary Nb-Cr-X phase diagrams were surveyed, and some interesting phase stability features were identified in these transition-metal systems. The average electron concentration factor (e/a) has been shown to be a dominant factor in controlling the phase stability of NbCr₂-based transition-metal Laves alloys. With $e/a \leq 5.76$, the C15 structure is stabilized; at an e/a range of 5.88-7.53, the C14 structure is stabilized; with $e/a \geq 7.65$, the C15 structure is stabilized again. A further increase in electron concentration ($e/a > 8$) leads to the disordering of the alloy. It is postulated that at $5.88 > e/a > 5.76$ and $7.65 > e/a > 7.53$, the C36 and other intermediate structures may be stabilized. Such an e/a correlation is found to be analogous to that in A₃B transition-metal intermetallic compounds and Mg-based Laves phases. An experimental investigation of ternary Nb-Cr-Cu systems indicates that the solubility of Cu in the NbCr₂ phase is as low as 1.3 at. %. Other phases, such as σ phase, a Cu-rich, and Nb-rich phase, can be stabilized in the Nb(Cr, Cu)₂ composition with 5 at. % Cu. However, within the solubility limit, the electron concentration/phase stability correlation is obeyed in this ternary system.

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Table 1. Atomic Size, Electron Concentration Factor (e/a) of Alloying Element, and Existing Binary Laves Phase

Element	Goldschmidt Radius (Å)*	e/a ⁺	XCr ₂ /NbX ₂
Nb	1.47	5	NbCr ₂
Ti	1.45	4	TiCr ₂
Ta	1.46	5	TaCr ₂
Cr	1.28	6	NbCr ₂
Mn	1.31	7	NbMn ₂
Fe	1.27	8	NbFe ₂
Co	1.26	9	NbCo ₂
Ni	1.24	10	None
Cu	1.28	11	None

* Data from Reference 16.

⁺ The unit of e/a is the number of electrons per atom in this paper.

Table 2. Atomic Size Ratio (R_A/R_B), Homogeneity Range (%A Range), Corresponding e/a Range and Laves Phase Structure in Binary XCr₂ and NbX₂ Alloy Systems

Laves Phase	R_A/R_B	%A Range	e/a Range	Structure
TiCr ₂	1.133	35-37	5.26-5.30	C15
TaCr ₂	1.141	33-36	5.64-5.67	C15
NbCr ₂	1.148	30-39	5.61-5.70	C15
NbMn ₂	1.122	25.5-40	6.20-6.49	C14
NbFe ₂	1.157	27-38	6.86-7.19	C14
NbCo ₂	1.167	27-33.3	7.67-7.92	C15
"NbNi ₂ "	1.185	33.3	8.34	None
"NbCu ₂ "	1.148	33.3	9.00	None

Table 3. Homogeneity Range (%X) and Corresponding e/a Range of C15/C14 Structures in Ternary Nb-Cr-X Systems

X	C15		C14		C15	
	%X	e/a	%X	e/a	%X	e/a
Ti	0-33.3	5.33-5.67	--	--	--	--
Ta	0-33.3	5.67	--	--	--	--
Fe	0-4	5.67-5.75	9-66.7	5.85-6.69	--	--
Co	0-3	5.67-5.76	8-62	5.91-7.53	66-68	7.65-7.72
Ni	0-2.5	5.67-5.77	5-52	5.87-8.05	--	--

Table 4 Chemical Compositions of Different Phases in Nb(Cr, Cu)₂ with 5 at. % Cu as Determined by Electron Microprobe

Phases	Point	Nb (at. %)	Cr (at. %)	Cu (at. %)
Matrix	1	34.11	64.57	1.32
	2	34.17	64.70	1.14
	3	33.94	64.94	1.12
	4	33.48	65.11	1.41
	5	34.09	64.55	1.37
	6	33.73	64.91	1.37
	Average	33.92	64.80	1.29
Bright Phase	1	50.46	46.24	3.30
	2	49.81	46.99	2.77
	3	49.97	46.98	3.05
	4	51.45	45.70	2.86
	5	49.78	47.11	3.11
	Average	50.29	46.60	3.02
Dark phase	1	0.26	2.87	96.87
	2	0.05	2.28	97.67
	3	0	2.49	97.51
	Average	0.10	2.55	97.35
Gray Phase	1	95.37	4.19	0.44

Figure Caption

Fig. 1 Effect of valence electron concentration on phase stability for several ternary Mg-based Alloys [reproduced after Ref. 1]

Fig. 2 Effect of average electron concentration (e/a) on phase stability in binary and ternary NbCr₂-based systems

Fig. 3 Effect of R_A/R_B ratio on the solubility range of binary Laves phases

Fig. 4 Effect of average electron concentration (e/a) on ordered structures in pseudo-binary Ni₃V-Co₃V and Co₃V-Fe₃V systems [Reproduced after Ref. 20]

Fig. 5 X-ray diffraction pattern of the Nb-61.6Cr-5Cu alloy, indexed as the C15 structure

Fig. 6 Microstructure of the Nb-61.6Cr-5Cu alloy, as-polished condition, (a) optical micrograph with polarized-light; (b) back-scattering electron micrograph. Phases 1, 2, 3 and 4 are Laves phase, σ -phase, Cu and Nb solid solutions, respectively.

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Fig. 3 Effect of R_A/R_B ratio on the solubility range of binary Laves phases

	(Co,Fe) ₃ V		(Co,Ni) ₃ V		(Co,Ni) ₃ V	
ALLOY	Fe ₃ V	↓	Co ₃ V	↓	↓	Ni ₃ V
e/a	7.25	<7.89	8.00	8.43	8.54	
STACKING SEQUENCE		ABC	ABCACB	ABCBCACAB	AB	
HEXAGONALITY		0	33.3	66.7	100	

Fig. 4 Effect of average electron concentration (e/a) on ordered structures in pseudo-binary Ni₃V-Co₃V and Co₃V-Fe₃V systems [Reproduced after Ref. 20]

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(b)

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